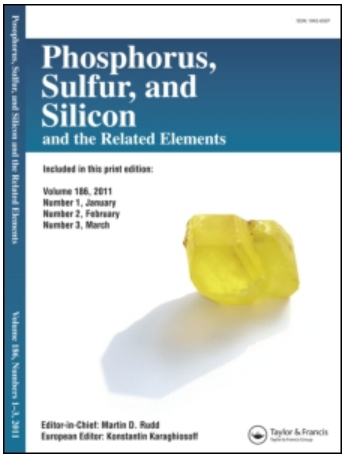

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PHOSPHORANES FORMED FROM THE CONDENSATION OF TRICO-ORDINATE PHOSPHORUS COMPOUNDS WITH PHENANATHRAQUINONE

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PHOSPHORANES FORMED FROM THE CONDENSATION OF TRICO-ORDINATE PHOSPHORUS COMPOUNDS WITH PHENANATHRAQUINONE

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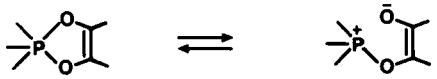
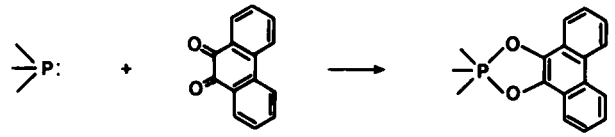
The synthesis of a range of monocyclic and bicyclic phosphoranes from the condensation of trico-ordinate phosphorus compounds with phenanthraquinone is reported together with their ^{31}P, ^{1}H and ^{13}C nmr data. The phosphorus chemical shifts of these compounds range from +34 to −35 ppm but solvent effects on δP and the retention of P–C coupling throughout the range indicate that all of these compounds are true phosphoranes.

The condensation of trico-ordinated phosphorus compounds with α-dicarbonyl compounds affords a useful synthetic route to a wide variety of cyclic oxyphosphoranes.[1–8] As a consequence of the large range of ^{31}P nmr shifts documented for oxyphosphorane species[9] there has been much debate as to whether compounds of type (**1**) are either classical pentaco-ordinate species, tetraco-ordinate zwitterions (**2**) or in some instances, an equilibrium mixture of both.



(1) (2)

Since we were aware that phenanthraquinone may give rise to bicyclic phosphoranes with low field chemical shifts ($ca + 30$)[10,11] it was decided to prepare a range of phosphoranes (**5**) from tricoordinate phosphorus compounds (**3**) and phenanthraquinone (**4**) and to elucidate their structures by a combination of ^{1}H, ^{13}C and ^{31}P nmr.



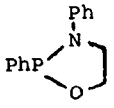
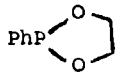
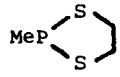
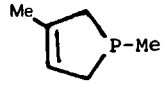
(3) (4) (5)

RESULTS AND DISCUSSION

The reactions were carried out in $CDCl_3$,C_6D_6 or C_7D_8 and were monitored by ^{31}P nmr. In each case a single phosphorus species was observed and a mass

TABLE I

^{31}P and ^{1}H nmr data of the PIII/PAQ adducts

P(III)	$\delta^{31}P$ of adduct $CDCl_3$	$\delta^{31}P$ of adduct C_6D_6	$\delta^{1}H$ of adduct ($CDCl_3$)
$Ph_2POCH_2CF_3$ (**3a**)	−20.6	−20.9	3.75–4.30 (dq $^3J_{FH}$ = 8 Hz, $^3J_{PH}$ = 7 Hz, 2H) 7.20–8.75 (m, 18H)
$PhP(OEt)_2$ (**3b**)	−34.7	−34.6	1.32(t, $^3J_{HH}$ = 7 Hz, 6H) 4.16 (dq, $^3J_{HH}$ = 7 Hz, $^3J_{PH}$ = 10 Hz, 4H) 7.16–8.84 (m, 13H)
Ph_2POEt (**3c**)	−17.0	−17.4[a]	1.32 (t, $^3J_{HH}$ = 7 Hz, 3H) 3.80 (dq, $^3J_{HH}$ = 7 Hz, $^3J_{PH}$ = 7 Hz, 2H) 7.16–8.75 (m, 18H)
$Ph_2PCH_2CH_2CN$ (**3d**)	−17.2	−17.5[a]	2.36–2.60 (m, 4H) 7.16–8.75 (m, 18H)
$PhP(OCH_2CF_3)_2$ (**3e**)	−31.9	−32.2	4.16–4.84 (m, 4H) 7.26–8.72 (m, 13H)
$(EtO)_3P$	−47.0	−47.3	1.29 (dt, $^3J_{HH}$ = 7 Hz, $^4J_{PH}$ = 1.6 Hz, 9H) 4.16 (dq, $^3J_{HH}$ = 7 Hz, $^3J_{PH}$ = 6.2 Hz, 6H) 7.14–8.68 (m, 8H)
 (3g)	−32.0	−32.5	2.38–2.76 (m, 2H) 3.35–3.80 (m, 2H) 7.05–8.70 (m, 18H)
 (3h)	−12.2	−12.4	3.78–4.12 (m, 4H) 7.10–8.63 (m, 13H)
 (3i)	+32.6	+33.6	2.56 (d, $^2J_{PH}$ = 13 Hz, 3H) 2.70–3.64 (m, 4H) 7.14–8.76 (m, 8H)
 (3j)	+17.5	+16.8	1.66 (d, $^2J_{PH}$ = 12.9 Hz, 3H) P—CH_3 1.80 (s, 3H) C—CH_3 2.10–2.70 (m, 4H) CH_2—P—CH_2— 6.46 (d, $^3J_{PH}$ = 30 Hz, 1H)—CH_2—CH=C— 7.43–8.60 (m, 8H)

[a] The solvent is C_7D_8.

spectrum of each reaction product revealed a parent peak for the adduct (**5**).† The ^{31}P and ^{1}H nmr data of the adducts are given in Table I and the ^{13}C data are reported in Table II.

It has been suggested[12,13] that compounds which resonate at high field in ^{31}P nmr (i.e. upfield of H_3PO_4) may actually be pentaco-ordinated species in rapid equilibrium with small amounts of the zwitterions. Conversely those materials with absorptions downfield of H_3PO_4 may be zwitterions in equilibrium with a small amount of the phosphorane species. Hence it would appear that

† The fragmentation patterns of the mass spectra showed features which were consistent with the proposed structures.

TABLE II

^{13}C n.m.r. data of the P(II)/PAQ adducts

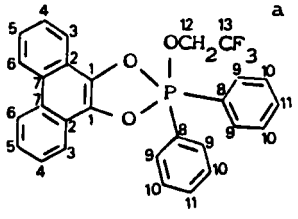
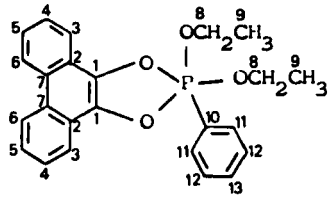
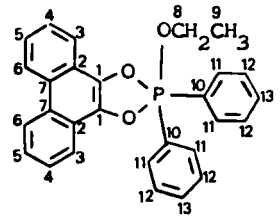
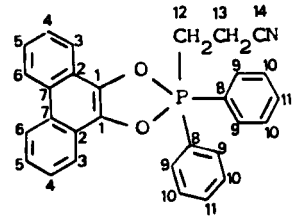
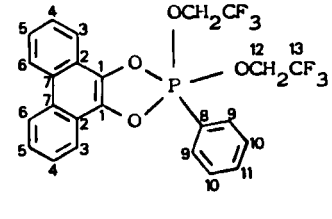
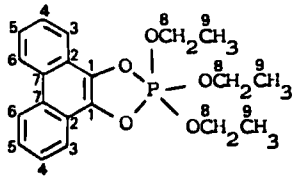
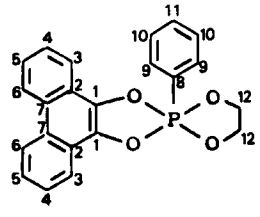
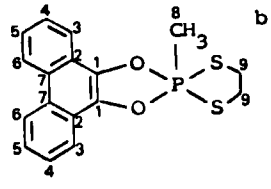
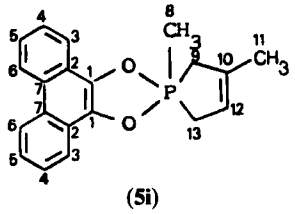
P(V)	$\delta^{13}C(CDCl)_3$	Assignment
 (5a)	61.9 (dq, $^2J_{CCF_3}$ = 35.5 Hz, ^2J_P = 7.8 Hz)	C-12
	120.6, 123.2, 124.5, 126.5, 126.8	C-3 to C-7
	122.4 (d, ^3J_P = 9.0 Hz)	C-2
	128.2 (d, ^3J_P = 16.7 Hz)	C-10
	131.5 (d, ^4J_P = 3.5 Hz)	C-11
	132.5 (d, ^2J_P = 11.7 Hz)	C-9
	134.1 (broad absorption)	C-1
	136.8 (d, ^1J_P = 185.4 Hz)	C-8
 (5b)	16.5 (d, ^3J_P = 7.6 Hz)	C-9
	62.8 (d, ^3J_P = 10.0 Hz)	C-8
	120.5, 123.1, 124.2, 126.3, 126.6	C-3 to C-7
	122.3 (d, ^3J_P = 10.0 Hz)	C-2
	127.6 (d, ^3J_P = 17.9 Hz)	C-12
	130.1 (d, ^4J_P = 3.0 Hz)	C-13
	130.5 (d, ^2J_P = 11.2 Hz)	C-11
	135.8 (s)	C-1
	138.7 (d, ^1J_P = 242.2 Hz)	C-10
 (5c)	16.6 (d, ^3J_P = 6.0 Hz)	C-9
	60.4 (d, ^2J_P = 8.8 Hz)	C-8
	120.7, 123.1, 124.0, 126.2, 126.5	C-3 to C-7
	122.7 (d, ^3J_P = 9.4 Hz)	C-2
	127.8 (d, ^3J_P = 15.9 Hz)	C-12
	130.7 (d, ^4J_P = 3.0 Hz)	C-13
	132.1 (d, ^2J_P = 11.1 Hz)	C-11
	136.5 (slightly broad absorption)	C-1
	137.5 (d, ^1J_P = 184.8 Hz)	C-10
 (5d)	13.3 (d, ^2J_P = 3.2 Hz)	C-13
	37.5 (d, ^1J_P = 71.0 Hz)	C-12
	120.1 (d ^3J_P = 18.1 Hz)	C-14
	120.7, 123.0, 124.1, 126.1, 126.6	C-3 to C-7
	122.7 (d, ^3J_P = 9.2 Hz)	C-2
	128.4 (d, ^3J_P = 13.9 Hz)	C-10
	129.7 (d, ^2J_P = 10.2 Hz)	C-9
	130.4 (d, ^4J_P = 2.5 Hz)	C-11
	132.5 (s)	C-1
	138.6 (d, ^1J_P = 125.0 Hz)	C-8
 (5e)	63.9 (dq, $^2J_{CCF_3}$ = 36.3 Hz, ^2J_P = 9.1 Hz)	C-12
	120.4, 123.4, 125.2, 126.9, 127.3	C-3 to C-7
	121.8 (d, ^3J_P = 10.6 Hz)	C-2
	123.5 (dq, ^1J_F = 278 Hz, ^3J_P = 10.6 Hz)	C-13
	128.2 (d, ^3J_P = 19.1 Hz)	C-10
	131.9 (d, ^4J_P = 7.1 Hz)	C-11
	132.1 (d, ^2J_P = 10.5 Hz)	C-9
	135.2 (d, ^1J_P = 241.8 Hz)	C-8
	135.4 (s)	C-1

TABLE II (*contd.*)

P(V)	$\delta^{13}C(CDCl)_3$	Assignment
 (5f)	16.4 (d, $^3J_P = 7.8$ Hz) 64.2 (d, $^2J_P = 9.0$ Hz 120.5, 123.2, 124.3, 126.3, 126.7 122.1 (d, $^3J_P = 13.5$ Hz) 134.8 (d, $^2J_P = 5.6$ Hz)	C-9 C-8 C-3 to C-7 C-2 C-1
 (5g)	60.2 (d, $^2J_P = 5.1$ Hz) 120.6, 123.0, 124.6, 126.6, 126.7 122.1 (d, $^3J_P = 11.6$ Hz) 128.4 (d, $^3J_P = 17.1$ Hz) 131.3 (d, $^4J_P = 3.3$ Hz) 131.5 (d, $^2J_P = 10.4$ Hz) 132.7 (d, $^1J_P = 213.3$ Hz) 134.7 (d, $^2J_P = 7.1$ Hz)	C-12 C-3 to C-7 C-2 C-10 C-11 C-9 C-8 C-1
 (5h) [b]	32.2 (d, $^1J_P = 111.3$ Hz) 34.2 (d, $^2J_P = 4.6$ Hz) 120.6, 123.0, 124.7, 126.6, 126.7 122.2 (d, $^3J_P = 9.6$ Hz) 135.8 (broad absorption)	C-8 C-9 C-3 to C-7 C-2 C-1
 (5i) [bc]	17.5 (d, $^1J_P = 86.5$ Hz) 20.7 (d, $^3J_P = 11.5$ Hz) 37.7 (d, $^1J_P = 71.3$ Hz) 40.2 (d, $^1J_P = 71.8$ Hz) 120.2 (d, $^3J_P = 18.0$ Hz) 120.5, 122.9, 123.6, 125.8, 126.3 123.0 (d, $^2J_P = 8.7$ Hz) 136.0 (d, $^2J_P = 2.8$ Hz)	C-8 C-11 C-9 C-13 C-2 C-3 to C-7 C-12 C-1

[a] C-13 not observed.
[b] No changes in coupling were observed on cooling to −50°. Identical spectra were obtained in deuteriotoluene.
[c] C-10 not observed.

(5a–h) are pentacovalent species by virtue of their high field negative chemical shifts whereas **(5i)** and **(5j)** could be zwitterions since they resonate at low field.

If an adduct were not a true phosphorane then it is reasonable to expect a significant variation in the ^{31}P chemical shift as the solvent is changed with a more polar solvent supporting the zwitterionic structure. In some instances (e.g. **6ab**) this phenomenon is observed.[1]

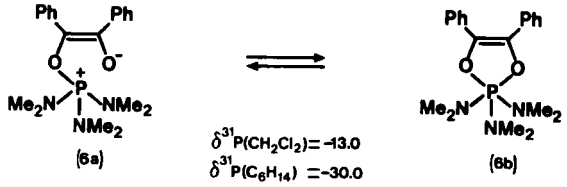
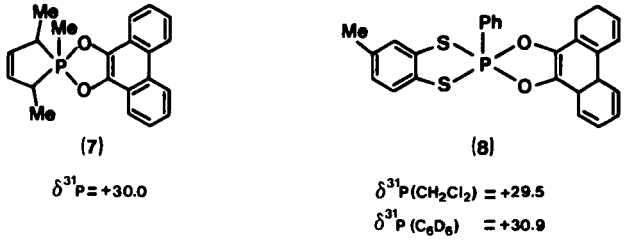
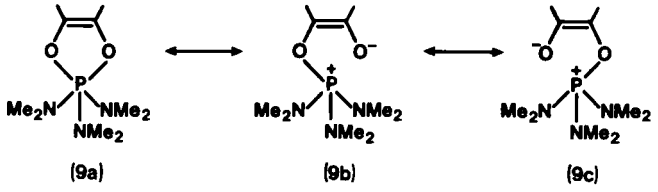


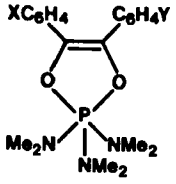
Table I shows that when the solvent was changed from toluene to the more highly polar chloroform there was no concomitant shift of the $\delta^{31}P$ values to lower field. This strongly suggests that *all* of the adducts studied, including (**5i**) and (**5j**) are pentacovalent structures with no contribution from equilibrated zwitterionic species. In support of this contention we have shown that the ^{31}P chemical shift of (**7**), which behaves as a phosphorane in terms of its fragmentation reactions,[10] is independent of solvent and Holmes[11] has reported a chemical shift for (**8**) in methylene chloride which is very close to that reported in benzene.[14]



Even if a change in chemical shift had been observed with a change in solvent however, Denney has suggested[6] that such changes can be explained equally well by considering (**9a–c**) as the canonical forms of a resonance hybrid with a greater contribution from (**9b** and **9c**) in polar media. This is evidenced by the fact that ^2J_P and ^3J_P couplings are observed in the ^{13}C nmr spectrum of (**9**) which is consistent *only* with the purely pentacovalent structure. Such couplings would not be expected in a rapidly equilibrating system.



Further studies by Denney on a series of substituted compounds (**10a–e**), arising from the reaction of $P(NMe_2)_3$ with a series of substituted benzils,[15] demonstrated that (**10ab**) were true phosphoranes by virtue of the *negative* ^{31}P chemical shifts and the strong ^3J_P phosphorus coupling to the *ipso*-carbons in the ^{13}C nmr spectra. However, in the case of (**10d**), the ^{31}P chemical shift was *positive* and ^3J_P coupling was lost indicating an ionic species. On cooling the coupling was also lost in (**10c**) and (**10e**) suggesting that these too are not true phosphoranes.



(10a–e)

a) X=Y = p–OMe
b) X=Y = p–Me
c) X=Y = p–F
d) X=Y = p–NO_2
e) X=H ; Y=p–Cl

The ^{13}C nmr spectral details of (**5a–f** and **5h–j**) are displayed in Table II. The adducts with negative ^{31}P chemical shifts, for which the assignment of the pentacovalent structure is not in dispute, display *equivalent* carbons (at C-1 and C-2) with the expected strong ^3J_P couplings ranging from 9.0 Hz to 13.5 Hz which are entirely consistent with literature values for well characterised oxyphosphoranes.[6] Furthermore (**5f**) and (**5h**) also show ^2J_P couplings to C-1 whereas several of the others exhibit broad absorptions for C-1 which may be indicative of very small (less that 1 Hz) couplings. In addition to carbons C-1 and C-2, all the other potentially equivalent carbons were found to be so. These observations are clearly explainable by a rapid intramolecular ligand reorganisation process for each molecule which, as Denney points out, does *not* need to invoke ionisation. In support of the existence of (**5i**) and (**5j**) as true phosphoranes both exhibited equivalent C-1 and C-2 carbons with strong ^3J_P couplings in their respective ^{13}C nmr spectra whose values did not vary on changing the solvent from chloroform to toluene. Furthermore (**5j**) showed a small ^2J_P coupling whereas the corresponding absorption in (**5i**) was slightly broad suggesting a small (<1 Hz) coupling. All the other potentially equivalent carbons were found to be so. The ^3J_P and ^2J_P couplings were retained on cooling to −50° and all other carbon resonances remained equivalent indicating once, again, that rapid ligand reorganisation is present in both cases with *no* evidence for ionisation.

One must conclude that (**5i**) and (**5j**), by virtue of the observed ^{13}C nmr evidence, exist as true pentacovalent species despite their positive $\delta^{31}P$ values.

1. *Instrumentation*

The ^{31}P nmr spectra were recorded on a Bruker HFX 90 FT instrument operating at 36.43 MHz and relative to 85% H_3PO_4 as standard with downfield shifts positive. The ^1H and ^{13}C nmr spectra were recorded on a Bruker WM 250 FT instrument operating at 250 MHz (protons) and 62.85 MHz (carbon) with TMS as internal standard.

2. *Starting materials*

Trico-ordinate phosphorus compounds (**3b**), (**3c**) and (**3f**) were obtained from commercial sources (Lancaster Synthesis or Maybridge Chem. Co.) and were redistilled prior to use. Compounds (**3g**) and (**3i**) were prepared as described previously[16] and literature methods were used to prepare (**3d**)[17,18] (**3h**)[19] and (**3j**).[20] Compound (**3a**) was prepared by the condensation of Ph_2PCl with 2,2,2-trifluoroethanol in THF at −15°C in the presence of triethylamine. After

removing the precipitated amine hydrochloride by filtration, the volatiles were evaporated from the filtrate under reduced pressure and the residual oil was distilled through a short Vigreux column to give a colourless oil (80% yield, b.p. 97.8° at 0.7 mm) with $\delta^{31}P(C_6D_6) = +126$ and $\delta^1H(CDCl_3)$, 4.15 (dq, $^3J_P = 8$) and 7.55 (m). Likewise compound (3e) was prepared from the reaction of $PhPCl_2$ with trifluorethanol to give 65% of a colourless oil, b.p. 63.4° at 0.35 mm with $\delta^{11}P = 166$ and $\delta^1H(CDCl_3)$, 4.13 (m, 4H) and 7.5 (m, 5H).

3. *Reaction of* (3) *with* (4); *general procedure*

An aliquot of the tricoordinated phosphorus compound (e.g. 1 mmol) was added to a suspension of (4,1 mmol) in deuteriochloroform (2 ml) or deuteriotoluene (2 ml) under an atmosphere of nitrogen. The mixture was shaken vigorously until the phenanthraquinone had dissolved and the spectra were taken immediately.

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REFERENCES

1. F. Ramirez, *Pure Appl. Chem.*, **9,** 337 (1964).
2. F. Ramirez, C. P. Smith, A. S. Gulati, and A. V. Patwardhan, *Tet. Lett.*, 2151 (1966).
3. F. Ramirez, A. V. Patwardhan, H. J. Kugler and C. P. Smith, *Tett. Lett.*, 3053 (1966).
4. F. Ramirez, C. P. Smith, J. F. Pilot and A. S. Gulati, *J. Org. Chem.*, **33,** 3787 (1968).
5. D. B. Denney, D. Z. Denney, D. M. Gavrilovic, P. J. Hammond, C. Huang and K. S. Tseng, *J. Amer. Chem. Soc.*, **102,** 7072 (1980).
6. D. B. Denney, D. Z. Denney, P. J. Hammond and K. S. Tseng, *J. Amer. Chem. Soc.*, 2054 (1981).
7. D. B. Denney, D. Z. Denney, P. J. Hammond, C. Huang, L. T. Liu and K. S. Tseng, *Phosphorus Sulphur,* **15,** 281 (1983).
8. M. R. Marre, J. F. Brazier, R. Wolf and A. Klaebe, *Phosphorus Sulphur,* **11,** 87 (1981).
9. J. Emsley and D. Hall, "The Chemistry of Phosphorus", Harper and Row, London (1976).
10. P. J. Hammond, J. Lloyd and C. D. Hall, *Phosphorus Sulphur,* **10,** 47 (1981).
11. R. Holmes and A. C. Sau, *J. Organometallic Chem.*, **156,** 253 (1978).
12. F. Ramirez, *Acc. Chem. Res.*, **1,** 168 (1968).
13. F. Ramirez, A. V. Patwardhan, H. J. Kugler and C. P. Smith, *Tetrahedgon,* **24,** 2275 (1968).
14. P. D. Beer, Ph.D. Thes, University of London (1982).
15. D. B. Denney and S. D. Pastor, *Phosphorus Sulphur,* **16,** 239 (1983).
16. P. D. Beer, R. C. Edwards, C. D. Hall, J. R. Jennings and R. J. Cozens, *Phosphorus Sulphur,* **17,** 283 (1983).
17. G. P. Schiemenz, *Chem. Ber.*, **98,** 514 (1966).
18. F. G. Mann and I. T. Millar, *J. Chem. Soc.*, 4453 (1952).
19. M. Wieber, J. Otto and M. Schmidt, *Angew. Chem. Int. Ed. Engl.*, **3,** 586 (1964).
20. L. D. Quin, J. P. Gratz and T. P. Barket, *J. Org. Chem.*, **33,** 1034 (1968).